

**SOUTH COAST AIR QUALITY MANAGEMENT DISTRICT**

**METHOD 100.1**

**INSTRUMENTAL ANALYZER PROCEDURES FOR CONTINUOUS GASEOUS  
EMISSION SAMPLING**

**TECHNICAL SUPPORT SERVICES  
APPLIED SCIENCE AND TECHNOLOGY  
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## **METHOD 100.1**

# **INSTRUMENTAL ANALYZER PROCEDURES FOR CONTINUOUS GASEOUS EMISSION SAMPLING**

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## METHOD 100.1

### INSTRUMENTAL ANALYZER PROCEDURES FOR CONTINUOUS GASEOUS EMISSION SAMPLING

#### Section 1 of 3

#### 1. Overview

##### 1.1 Principle

A representative sample of an exhaust gas stream is continuously extracted, conditioned, and conveyed to instrumental analyzers for the determination of:

- Sulfur dioxide ( $\text{SO}_2$ ) gas concentrations using an ultraviolet (UV) or a non-dispersive ultraviolet (NDUV) analyzer.
- Oxides of nitrogen ( $\text{NO}_x$ ) gas concentrations using a chemiluminescent analyzer.
- Oxygen ( $\text{O}_2$ ) gas concentrations using an electrochemical (fuel cell) type analyzer.

- Carbon monoxide (CO) gas concentrations using a non-dispersive infrared (NDIR) analyzer.
- Carbon dioxide (CO<sub>2</sub>) gas concentrations using a non-dispersive infrared (NDIR) analyzer.

Other systems may be used to measure SO<sub>2</sub>, NO<sub>x</sub>, O<sub>2</sub>, CO, and CO<sub>2</sub> if they meet the specifications of this method and have been subjected to a relative accuracy test to determine equivalence.

Performance specifications and test procedures are provided to ensure reliable data. Typical analyzer specifications are shown in Table 100.1-1.

## 1.2 Applicability

This method measures emissions of SO<sub>2</sub>, NO<sub>x</sub>, O<sub>2</sub>, CO, and CO<sub>2</sub> from stationary source gas streams flowing in ducts, stacks, and flues. This procedure does not supersede the New Source Performance Standards (NSPS) requirement for permanently installed continuous monitoring instruments.

This test procedure is an alternative to SCAQMD reference methods, in particular SCAQMD Methods 3.1, 6.1, 7.1, and 10.1. It should be used only on sources where its equivalency to the reference methods has been established, or where specific regulations for the source specify this procedure.

### 1.3 Range and Sensitivity

#### 1.3.1 Analytical Range

The analytical range is selected so that the sample gas concentration for each run is between 20 and 95 percent of the range, for 95 percent of the test period. The run is considered invalid if the measured gas concentration exceeds the range during the test period. Data obtained below 20 percent of the range can be used only for qualitative purpose.

#### 1.3.2 Sensitivity

The minimum detectable limit depends on the analytical range, span, and signal-to-

noise ratio of the measurement system.

For a well designed system, the minimum detectable limit shall be less than 2 percent of the range.

## METHOD 100.1

# INSTRUMENTAL ANALYZER PROCEDURES FOR CONTINUOUS GASEOUS EMISSION SAMPLING

### Section 2 of 3

## 2. Field Procedures

### 2.1 Definitions

#### 2.1.1 Measurement System

Equipment required to determine sample gas concentration consists of three major sub-systems:

Sample Interface - The portion of the system used for sample acquisition, sample transport, sample conditioning, and protection of the analyzers from the effects of the stack effluent.

Gas Analyzer - The portion of the system that identifies the gas component and generates an output proportional to its concentration.

Data Acquisition - A strip chart recorder, analog computer and printer, or any combination thereof, for recording measurement data from the analyzer output.

2.1.2 Range

The upper limit of the gas concentration measurement range displayed on the data recorder.

2.1.3 Calibration Gas

A gas of known concentration in an inert diluent gas.

2.1.4 Analyzer Calibration Error

The difference between the known concentration of the calibration gas and the gas concentration exhibited by the gas analyzer when the calibration gas is introduced directly to the analyzer.

#### 2.1.5 Sampling System Bias

The difference between the gas concentrations exhibited by the measurement system when calibration gas is introduced at the sampling probe tip filter and when the same calibration gas is introduced directly to the analyzer.

#### 2.1.6 Zero Drift

The difference in the measurement system responses at a zero concentration level during the initial calibration, and final calibration check after a test. During this test there should be no unscheduled maintenance, repair, or adjustment of the measurement system.

#### 2.1.7 Calibration Drift

The difference in the measurement system responses at a mid-range concentration level during the initial calibration, and final calibration check after a test. During this test there should be no

unscheduled maintenance, repair, or adjustment of the measurement system.

#### 2.1.8 Response Time

The time required for the system to display 95 percent of a step change in gas concentration on the data recorder.

#### 2.1.9 Interference Response

The output response of the measurement system to a component in the sample gas, other than the gas component being measured.

#### 2.1.10 Calibration Curve

A graph or other systematic method of establishing the relationship between the analyzer response and the actual calibration gas concentration introduced to the analyzer.

#### 2.1.11 Linearity

Maximum deviation as a percent of range, between a mid-range calibration reading and the reading predicted by a straight line drawn between high-range and zero gas calibration points.

### 2.2 Measurement System Performance Specifications

#### 2.2.1 Analyzer Calibration Error

Less than  $\pm 2$  percent of the range for the zero, mid-range, and high-range calibration gases.

#### 2.2.2 Sampling System Bias

Less than  $\pm 5$  percent of the range for the zero, and mid-or high range calibration gases.

#### 2.2.3 Zero Drift

Less than  $\pm 3$  percent of the range over the period of each run.

#### 2.2.4 Calibration Drift

Less than  $\pm 3$  percent of the range over the period of each run.

#### 2.2.5 Interference Response

Each of the analyzers described shall have the following minimum interference response to the gases listed. For example, an SO<sub>2</sub> analyzer should respond no more than 30 ppm when the NO<sub>2</sub> concentration in the sample gas is 2000 ppm.

##### SO<sub>2</sub> Analyzer

NO<sub>2</sub> 2,000/30

NH<sub>3</sub> 10<sup>6</sup>/0

##### CO<sub>2</sub> Analyzer

H<sub>2</sub>O 10,000/1

CO 15,000/1

CH<sub>4</sub> 20,000/1

##### CO Analyzer

H<sub>2</sub>O 200,000/1

CO<sub>2</sub> 500,000/1

SO<sub>2</sub> 10<sup>6</sup>/1

NO  $10^6/1$

NO<sub>2</sub>  $10^6/1$

HC  $10^6/1$

N<sub>2</sub>O  $10^3/1$

#### 2.2.6 Linearity

Less than  $\pm 1.0$  percent of the range for the pretest and post test values.

### 2.3 Apparatus and Measurement System

A schematic of an acceptable measurement system is shown in Figures 100.1-1, 100.1-2, and 100.1-3. The essential components of the measurement system are described below.

#### 2.3.1 Probe

Use quartz, borosilicate glass, stainless steel, aluminum oxide, porcelain, Hastalloy, or Inconel tubing of approximately 1/4 inch diameter or larger. If stack temperatures are above 1200°F the probe should be designed to minimize the time the sample is kept at those high temperatures. Use a heated probe if condensation occurs.

### 2.3.2 Sample Line

Use Teflon or stainless steel tubing to transport the sample gas to the moisture removal system. The sampling line should be heated to prevent condensation. If the sample passes through a moisture knockout trap immediately after extraction from the stack, it is not necessary to heat the sample transport line downstream of the moisture removal trap. A sample line made from another material may be used if the material does not absorb, adsorb, evolve, or alter the pollutants being monitored.

### 2.3.3 Probe Calibration System

Calibration gases should be introduced into a baffled sample chamber around the probe tip filter when in the probe calibration mode.

#### 2.3.4 Sample Conditioning

- a. The sample conditioner should be capable of reducing moisture content to below a dewpoint of 35°F.
- b. All parts exposed to the sample should be glass, stainless steel, or Teflon.
- c. Remove water by using refrigeration or a permeation dryer designed to minimize contact between the condensate and sample gas.
- d. Provide for back flushing the probe filter with zero air to remove particulate buildup on the probe filter.

#### 2.3.5 Sample Transport Lines

Use Teflon or stainless steel lines to transport the sample from the moisture removal system to the sample pump, sample flow rate control, and sample gas manifold.

#### 2.3.6 Particulate Filter

Use an in-stack 5 micron stainless steel or Inconel 600 porous filter or a heated (sufficient to prevent water condensation) out-of-stack filter. The out-of-stack filter should be borosilicate or quartz glass wool or glass fiber mat. Additional filters at the inlet or outlet of the moisture removal system and inlet of the analyzer may be used to prevent accumulation of particulate material in the measurement system, and to extend the useful life of the components. All filters should be fabricated of materials that are nonreactive to the gas being sampled.

#### 2.3.7 Sample Pump

Use a leak-free pump to pull the sample gas through the system at a flow rate sufficient to minimize the response time of the measurement system. The pump may be constructed of any material that is nonreactive to the gas being sampled.

#### 2.3.8 Sample Flow Rate Control

Use a control valve and rotameter to maintain a sampling rate constant within 10 percent.

The tester may elect to install a back pressure regulator to maintain the sample gas manifold at a constant pressure in order to protect the analyzers from over pressurization or the need for flow rate adjustments.

#### 2.3.9 Sample Gas Manifold

Use a sample gas manifold to divert a portion of the sample gas stream to the analyzer, and the remainder to the bypass discharge vent. The sample gas manifold also should include provisions for introducing calibration gases directly into the analyzer. The manifold may be constructed of any material that is nonreactive to the gas being sampled.

#### 2.3.10 Gas Analyzer

Use a gas analyzer to continuously determine the  $\text{SO}_2$ ,  $\text{NO}_x$ ,  $\text{O}_2$ ,  $\text{CO}_2$ , or  $\text{CO}$  concentration in the sample gas stream. Each analyzer should meet the applicable performance specifications of Section 2.2. Each analyzer should be provided with a means of controlling its flow rate and a device for determining proper sample flow rate (e.g. precision rotameter, pressure gauge downstream of all flow controls).

An  $\text{NO}_2$  to  $\text{NO}$  converter in an  $\text{NO}_x$  analyzer is the portion of the system that converts nitrogen dioxide ( $\text{NO}_2$ ) in the sample gas to nitric oxide ( $\text{NO}$ ). An  $\text{NO}_2$  to  $\text{NO}$  converter is not necessary if data are presented to demonstrate that the  $\text{NO}_2$  portion of the exhaust gas is less than 5 percent of the total  $\text{NO}_x$  concentration. A high temperature ( $650^\circ\text{C}$ ) stainless steel converter should be used when no  $\text{NH}_3$  is present and a low temperature ( $350^\circ\text{C}$ ) molybdenum converter should be used when

$\text{NH}_3$  is present. Other converters may be used if equivalence is demonstrated.

Housing the analyzer in a clean, thermally-stable, vibration-free environment will minimize drift in the analyzer calibration.

#### 2.3.11 Data Recorder

Use a strip chart recorder, analog computer, or digital recorder, for recording measurement data. The data recorder resolution, or readability should be 0.5 percent of range. Sampling measurements should be obtained at a minimum of 1 minute intervals.

#### 2.3.12 Interference Response Sampling System

Introduce an interference test gas to the analyzer. The analyzer zero should be given a positive offset prior to the test to allow measurement of a negative interference. As an alternative, offset chart paper may be used to avoid changing the analyzer zero.

#### 2.3.13 Pitot Tubes

Same as required by SCAQMD Methods 1.1 and 2.1.

#### 2.3.14 Differential Pressure Gauge

Same as required by SCAQMD Methods 1.1 and 2.1.

#### 2.3.15 Sample Gas Moisture Content Equipment

As specified by SCAQMD Method 4.1.

#### 2.3.16 Barometer

Use a mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 0.1 in. Hg.

#### 2.3.17 Vacuum Gauge

Use a 30 in. Hg gauge for leak checking the sampling system.

### 2.3.18 Thermocouple

Use a Type K thermocouple to measure the temperature of the stack gas.

## 2.4 Calibration Gases

Calibration gases shall be certified according to EPA Traceability Protocol Number 1 (see Table 100.1-2 for cylinder gas recertification schedule) or certified to an analytical accuracy of  $\pm 1$  percent and be traceable to applicable NBS Standard Reference Materials (SRM's).

Traceability shall include identification of applicable SRM and its cylinder number. Super blends, i.e. gas mixtures of nitric oxide, sulfur dioxide, carbon monoxide and carbon dioxide with nitrogen as the balance gas, may be used for simultaneous calibration of multiple analyzers. The average deviation of each component gas shall not exceed  $\pm 1$  percent of the tag value, and shall be confirmed using NBS traceable standards within six month intervals.

EPA Traceability Protocol No. 1 is in the Appendix.

Use three calibration gases as specified below:

2.4.1 High-Range Gas

The concentration should be equivalent to 80 to 100 percent of the range.

2.4.2 Mid-Range Gas

The concentration should be equivalent to 40 to 60 percent of the range.

2.4.3 Zero Gas

The impurity concentration should be less than 0.25 of one percent of the range.

Purified ambient air may be used for the zero gas by passing compressed air through a heatless dryer, a catalytic oxidizer, and a carbon dioxide scrubber.

Use ultra zero grade nitrogen gas for zeroing the  $O_2$  analyzer.

## 2.5 Measurement System Performance Test Procedures

Perform the following procedures before measurement of emissions (Section 2.6).

### 2.5.1 Cleaning of Sample Train

As needed, thoroughly flush the probe, heat-trace line, and sample conditioner with distilled water, followed by acetone. Dry with filtered dry air.

### 2.5.2 Continuous Analyzers

Allow analyzers to warm up according to manufacturer's instructions.

### 2.5.3 Sampling System Preparation

A leak check of the sampling system is a good practice. However, it is optional.

Assemble the sample train as shown in Figures 100.1-1, 100.1-2 and 100.1-3.

Leak check the vacuum side of the assembly to a minimum of 20 inches of Hg (gauge).

The sampling system should hold 20 inches of Hg vacuum for 5 minutes with less than 1 in. Hg loss. Correct any leaks found and repeat the leak check until a satisfactory result is obtained. Check the pressure side of the system with liquid soap solution and correct any leaks. Alternative leak check methods are acceptable if equivalent or better than the specified method.

The sample train assembly may be modified as follows to reflect actual stack conditions:

- If the stack is at or below ambient temperature and condensation is not observed upstream of the sample conditioner, the probe heating element and the heat trace line can be eliminated.
- If only concentration measurements are required, the Pitot tube can be eliminated.

Introduce zero and high range calibration gases directly to the instruments and make all necessary adjustments to calibrate the analyzer and the data recorder. Adjust system components to achieve individual analyzer sampling rates recommended by the instrument manufacturer.

#### 2.5.4 Analyzer Calibration Error

Conduct the analyzer calibration error check at the beginning and end of each test run by introducing calibration gases to the measurement system at any point upstream of the gas analyzer as follows:

- a. After the measurement system has been prepared for use, introduce the zero, mid-range, and high-range gases to the analyzer. During this check, make no adjustments to the system except those necessary to achieve the correct calibration gas flow rate at the analyzer. Record the analyzer responses to each calibration gas on a form similar to Figure 100.1-4.

The calibration error check should be considered invalid if the gas concentration displayed by the analyzer exceeds  $\pm 2$  percent of the range for any of the calibration gases. If an invalid calibration is exhibited, take corrective action and repeat the analyzer calibration error check until acceptable performance is achieved.

#### 2.5.5 Instrument Response Time

Establish during semi-annual certification.

#### 2.5.6 Sampling System Bias Check

A bias check of the sampling system is mandatory.

Backflush gas through the probe as necessary to prevent particulate buildup on the probe filter. Perform the sampling system bias check by introducing calibration gases into a baffled sample chamber around the probe tip filter.

A zero gas and either the mid-range or high-range gas, whichever most closely approximates the effluent concentrations, should be used for this check as follows:

- a. Introduce the upscale calibration gas and record the gas concentration displayed by the analyzer on a form similar to Figure 100.1-5. Introduce the zero gas and record the gas concentration displayed by the analyzer. During the sampling system bias check operate the system at the normal sampling rate and make no adjustments to the measurement system other than those necessary to achieve manufacturer recommended calibration gas flow rates at the analyzer.
- b. The sampling system bias check shall be considered invalid if the difference between the gas concentrations exhibited by the measurement system when a known concentration gas is introduced at the sampling probe tip and when the same

gas is introduced directly to the analyzer, exceeds  $\pm 5$  percent of the analyzer range. If an invalid calibration is exhibited, take corrective action and repeat the sampling system bias check until acceptable performance is achieved.

If adjustment to the analyzer is required, first repeat the analyzer calibration error check, then repeat the sampling system bias check.

#### 2.5.7 NO<sub>2</sub> to NO Conversion Efficiency

Conduct an NO<sub>2</sub> to NO conversion efficiency test in accordance with EPA Method 20 or by using an NBS traceable gas mixture of NO<sub>2</sub> in air.

### 2.6 Emission Test Procedure

Traverse the duct to determine if there is stratification (see Chapter X). Single point gas sampling is acceptable if the gas composition is homogeneous, i.e.  $< 10$  percent variation between any two traverse points in the gas stream

throughout the cross sectional diameter of the stack. For multipoint gas sampling use every other point, as required by SCAQMD Method 5.1 for particulate matter. Determine moisture content and velocity pressures in the stack gas according to SCAQMD Methods 1.1, 2.1 and 4.1 if required for mass flow rate calculations. The probe inlet should never be closer than one inch to the stack wall. As an alternate method, the mass flow rate may be obtained by stoichiometric and gas composition relations.

#### 2.6.1 Chart Recorder Label

Turn on strip chart recorder and label the chart as to pollutant, source, range, calibration cylinder ID number, certified expiration date, zero and upper range calibration settings, chart speeds, date, time, person operating instruments, and other pertinent data.

#### 2.6.2 Sample Probe Traverse and Minimum Sampling Time

Insert the sample probe assembly into the stack and blank off the remainder of the

opening. Conduct a gas sample traverse to determine if single point sampling is acceptable and label the response obtained on the strip chart. If a traverse is required, leave the probe at each traverse point for at least the system response time plus one minute, allowing enough time for the system to be flushed and the instruments to respond fully. Move the probe to the next traverse point and repeat. Continue until the stack has been fully traversed.

A minimum sample time of 60 minutes is recommended. See District Rules and Regulations and permit conditions for applicable requirements. When the test duration exceeds one hour, conduct zero and span checks every 2 hours. Adjust settings as necessary, mark strip charts, and record in log books.

#### 2.6.3 Zero and Calibration Drift Tests

Immediately preceding and following each run, or if adjustments are necessary for the measurement system during the run,

repeat the sampling system bias check procedure. (Make no adjustments to the measurement system until after the drift checks are completed.) Record the analyzer's responses on a form similar to Figure 100.1-5.

2.6.3.1 If either the zero or upscale calibration value exceeds the sampling system bias specification, then the run is considered invalid. Repeat both the analyzer calibration error check procedure and the sampling system bias check procedure before repeating the run.

2.6.3.2 If both the zero and upscale calibration values are within the sampling system bias specification, then use the average of the initial and final bias check values to calculate the gas concentration for the run. If the zero or upscale calibration drift value exceeds the drift limits, based on the

difference between the sampling system bias check responses immediately before and after the run, repeat both the analyzer calibration error check procedure and the sampling system bias check procedure before conducting additional runs.

#### 2.6.4 Post Run Leak Check

If a prerun leak check is conducted, proceed as follows:

See Section 2.5.3. If the leak rate is 2 percent or more of the total sample flow rate (approximately 0.4 SCFH) discard the test.

#### 2.7 Emission Calculation

Determine the average gas effluent concentration from the average gas concentration displayed by the gas analyzer and adjust for zero and high range calibration drift. The average gas concentration displayed by the analyzer may be determined by integration of the area under the

curve for chart recorders, or by averaging all of the effluent measurements. Alternatively, the average may be calculated from measurements recorded at equally spaced intervals over the entire duration of the run. Sampling measurements should be obtained at a minimum of 1 minute intervals. Calculate the effluent gas concentration using the following equation:

$$C_{\text{gas}} = (\bar{C} - C_o) \frac{C_{\text{ma}}}{C_m - C_o}$$

where:

$C_{\text{gas}}$  = Effluent gas concentration, dry basis, ppm

$\bar{C}$  = Average gas concentration indicated by gas analyzer, dry basis, ppm

$C_{\text{ma}}$  = Actual concentration of the upscale calibration gas, ppm

$C_m$  = Average of initial and final system calibration bias check responses for the upscale calibration gas, ppm

$C_0$  = Average of initial and final system  
calibration bias check responses for the  
zero gas, ppm

## METHOD 100.1

### INSTRUMENTAL ANALYZER PROCEDURES FOR CONTINUOUS GASEOUS EMISSION SAMPLING

#### Section 3 of 3

### 3. Calculations and Reporting

#### 3.1 Emission Rate of Gas

$$E = \frac{(C_g)(M)}{379 \times 10^6} (Q)(60)$$

where:

E = Emission rate, lb/hr

C<sub>g</sub> = Concentration of gas, ppm

M = Molecular weight of gas\*, lb/lb-mole

Q = Stack Effluent, dscfm

60 = Conversion factor, min/hr

379 x 10<sup>6</sup> = Conversion factor, scf/lb-mole

\*NO<sub>x</sub> is often expressed as NO<sub>2</sub>

### 3.2 Percent Excess Air

$$EA = \frac{[O_2 - 0.5 CO]}{[0.264 N_2 - (O_2 - 0.5 CO)]} \times 100$$

where:

EA = Percent excess air

O<sub>2</sub> = Percent O<sub>2</sub> by volume, dry basis  
(measured)

CO = Percent CO by volume, dry basis  
(measured)

N<sub>2</sub> = Percent N<sub>2</sub> by volume, dry basis  
(calculated)

0.264 = Ratio of O<sub>2</sub> in air, v/v

### 3.3 Pollutant Concentration Calculated to 12 Percent CO<sub>2</sub>, 3 Percent O<sub>2</sub>, and 15 Percent O<sub>2</sub>

Concentration<sub>(12 Percent O<sub>2</sub>)</sub> =

$$\text{Concentration}_{(\text{std})} \times \frac{12}{CO_2} \quad (\text{measured})$$

CO<sub>2</sub> = Percent CO<sub>2</sub> by volume, dry basis

Concentration<sub>(3 Percent O<sub>2</sub>)</sub> = Concentration<sub>(std)</sub>

$$\text{Concentration}_{(\text{std})} \times \frac{20.9 - 3.0}{20.9 - O_2} \quad (\text{measured})$$

Concentration<sub>(15 Percent O<sub>2</sub>)</sub> = Concentration<sub>(std)</sub>

$$\text{Concentration}_{(\text{std})} \times \frac{20.9 - 15.0}{20.9 - \text{O}_2 \text{ (measured)}}$$

Based on O<sub>2</sub> in air as 20.9 percent.

TABLE 100.1-1

## Analyzer Specifications for Continuous Gaseous Emission Stack Sampling

	Sulfur Dioxide	Oxides of Nitrogen	Carbon Monoxide	Carbon Dioxide	Oxygen
Typical Principle of Operation (1)	Ultra-Violet or Non-Dispersive Ultra-Violet Absorption Photometry	Chemiluminescence	Non-Dispersive Infrared Absorption	Non-Dispersive Infrared Absorption	Electro-chemical
Typical Range of Concentration	50, 250, 1000 ppm	10, 25, 100, 250, 1000, 10,000 ppm	5, 10, 50, 500, 2500, 5000 ppm	2, 10, 20 Percent	5, 10, 25 Percent
Sensitivity, Minimum Detectable Limit, Percent of Full Scale	2.0	2.0	2.0	2.0	2.0
Noise Level, Percent of Full Scale (Peak to Peak)	$< \pm 1.0$	$< \pm 1.0$	$< \pm 1.0$	$< \pm 1.0$	$< \pm 1.0$
Response Time, Time Interval from a Step Change in Input Concentration at Inlet to Instrument to Output Reading of 95 Percent of Steady State	10 Seconds	3 Seconds	10 Seconds	10 Seconds	10 Seconds

TABLE 100.1-1 Cont.

	Sulfur Dioxide	Oxides of Nitrogen	Carbon Monoxide	Carbon Dioxide	Oxygen
Analyzer Calibration Error, Percent of Range for the Zero, Mid-Range, and High-Range Calibration Gases	$< \pm 2.0$	$< \pm 2.0$	$< \pm 2.0$	$< \pm 2.0$	$< \pm 2.0$
Zero Drift, Percent of Range over the Period of Each Run	$< \pm 3.0$	$< \pm 3.0$	$< \pm 3.0$	$< \pm 3.0$	$< \pm 3.0$
Calibration or Span Drift, Percent of Range over the Period of Each Run	$< \pm 3.0$	$< \pm 3.0$	$< \pm 3.0$	$< \pm 3.0$	$< \pm 3.0$
Precision, Maximum Avg. Deviation from Mean Change as Percent of Range	$< \pm 1.0$	$< \pm 1.0$	$< \pm 1.0$	$< \pm 1.0$	$< \pm 1.0$

TABLE 100.1-1 Cont.

	Sulfur Dioxide	Oxides of Nitrogen	Carbon Monoxide	Carbon Dioxide	Oxygen
Linearity (2)	$< \pm 1.0$	$< \pm 1.0$	$< \pm 1.0$	$< \pm 1.0$	$< \pm 1.0$
Interference Response	$\text{NO}_2$ 2000/30 $\text{NH}_3$ $10^6/0$		$\text{H}_2\text{O}$ 200,000/1 $\text{CO}_2$ 500,000/1 $\text{SO}_2$ $10^6/1$ $\text{NO}$ $10^6/1$ $\text{NO}_2$ $10^6/1$ $\text{HC}$ $10^6/1$ $\text{N}_2\text{O}$ $10^3/1$	$\text{H}_2\text{O}$ 10,000/1 $\text{CO}$ 15,000/1  $\text{CH}_4$ 20,000/1	

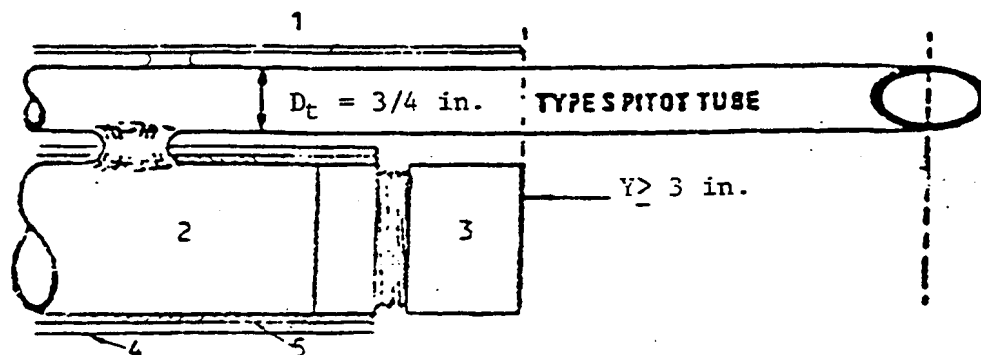
(1) Other types may also be acceptable.

(2) Maximum deviation between a mid-range calibration reading and the reading predicted by a straight line drawn between high-range and zero gas calibration points, as a percent of range.

TABLE 100.1-2

## Cylinder Gas Recertification Schedule

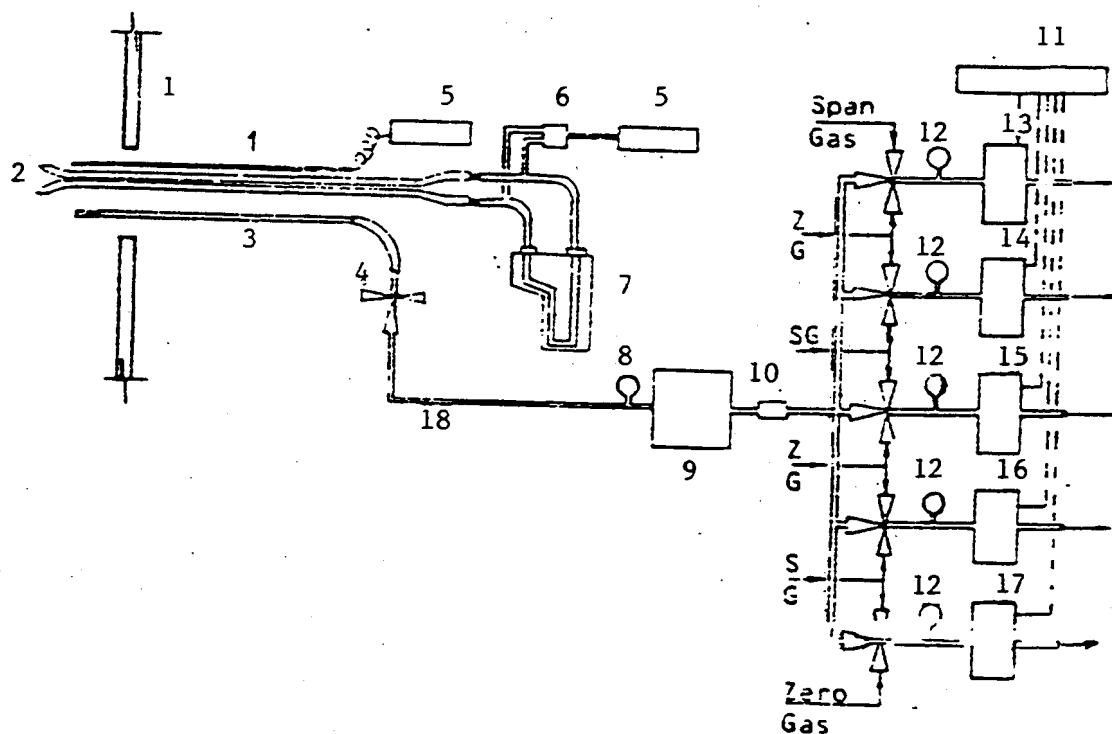
Pollutant	Balance Gas	Concentration Range	Maximum Months Until Recertification for Cylinder Material:	
			Al or SS	Other
Carbon Monoxide	N <sub>2</sub> or Air	≥ 5 ppm	18	6
Nitric Oxide	N <sub>2</sub>	≥ 10 ppm	18	6
Sulfur Dioxide	N <sub>2</sub>	≥ 10 ppm	18	6
Nitrogen Dioxide	N <sub>2</sub> or Air	≥ 10 ppm	6	6
Carbon Dioxide	N <sub>2</sub> or Air	≥ 300 ppm	18	18
Oxygen	N <sub>2</sub>	≥ 2 %	18	18
Sulfur Dioxide and Carbon Dioxide	N <sub>2</sub>	≥ 200 ppm SO <sub>2</sub> , ≥ 10 %	18	6
Propane	N <sub>2</sub> or Air	≥ 5 ppm	18	6
Others not Specifically Listed			6	6



1. Thermocouple
2. Sample Probe
3. Probe Filter
4. Probe Shield
5. Heating Element

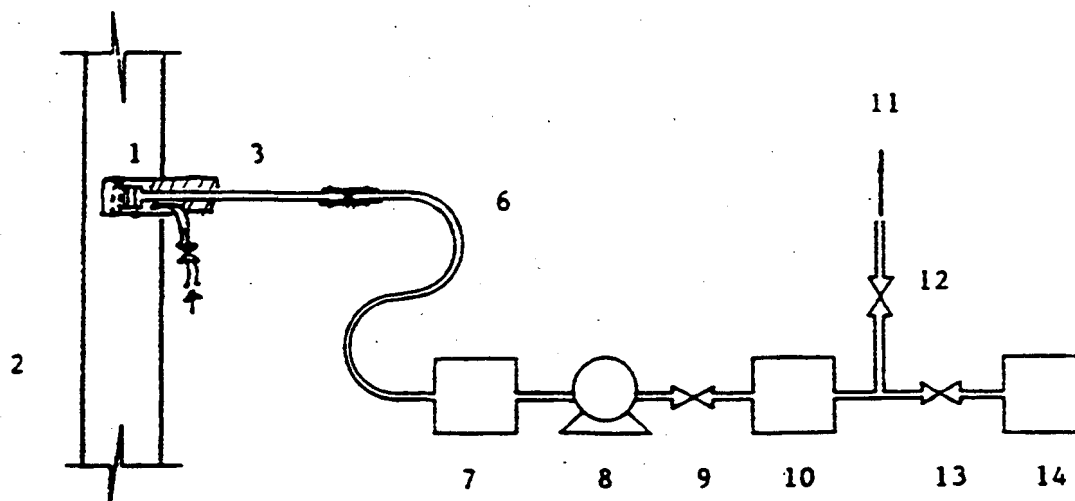
Figure 100.1-1

Sample Probe Assembly



- |                        |                              |
|------------------------|------------------------------|
| 1. Stack               | 9. Sample Conditioner        |
| 2. Pitot Tube          | 10. Filter                   |
| 3. Probe Assembly      | 11. Multichannel Recorder    |
| 4. Three Way Valve     | 12. Flow Meter               |
| 5. Recorder            | 13. O <sub>2</sub> Analyzer  |
| 6. Pressure Transducer | 14. CO Analyzer              |
| 7. Manometer           | 15. CO <sub>2</sub> Analyzer |
| 8. Pressure Gauge      | 16. NO <sub>x</sub> Analyzer |
|                        | 17. SO <sub>2</sub> Analyzer |
|                        | 18. Heat Trace Sample Line   |

Figure 100.1-2  
Sample Train Assembly



- 1. Filter
- 2. Stack
- 3. Probe
- 4. Calibration Valve
- 5. Calibration Gas Inlet
- 6. Heated Sample Line
- 7. Moisture Removal System

- 8. Pump
- 9. Flow Control Valve
- 10. Sample Gas Manifold
- 11. Sample Bypass Discharge
- 12. By pass Flow Control
- 13. Analyzer Flow Control
- 14. Gas Analyzer

Figure 100.1-3  
Measurement System Schematic

Date\_\_\_\_\_

Analyzer\_\_\_\_\_

Range\_\_\_\_\_

	Cylinder value (indicate units)	Analyzer calibration response (indicate units)	Absolute differ- ence (indicate units)	Differ- ence (percent of range)
Zero gas				
Mid-range gas				
High-range gas				

Pretest Linearity Error \_\_\_\_\_ percent range

Post Test Linearity Error \_\_\_\_\_ percent range

Figure 100.1-4  
Analyzer Calibration Data Form

Date \_\_\_\_\_

Analyzer \_\_\_\_\_

Range \_\_\_\_\_

	Analyzer calibra- tion response	Initial Values		Final Values		Drift
		System calibra- tion response	System calibra- tion bias (percent of range)	System calibra- tion response	System calibra- tion bias (percent of range)	(percent of range)
Zero gas						
High-range gas						

System Calibration Bias =

$$\frac{\text{System Calibration Response} - \text{Analyzer Calibration Response}}{\text{Range}} \times 100$$

Drift =

$$\frac{\text{Final System Calibration Response} - \text{Initial System Calibration Response}}{\text{Range}} \times 100$$

Figure 100.1-5  
System Calibration Bias and Drift Data

## **APPENDIX**

3.0.4. PROCEDURE FOR NBS-TRACEABLE CERTIFICATION OF COMPRESSED  
GAS WORKING STANDARDS USED FOR CALIBRATION AND  
AUDIT OF CONTINUOUS SOURCE EMISSION MONITORS  
(Revised Traceability Protocol No. 1)

CONTENTS

<u>Subsection</u>	<u>Title</u>	<u>Pages</u>
3.0.4.0	General Information	1 to 8
3.0.4.1	<u>Procedure G1</u> : Assay and Certification of a Compressed Gas Standard Without Dilution	G1-1 to G1-5
3.0.4.2	References	

4.0 GENERAL INFORMATION

4.0.1 Purpose and Scope of the Procedure

Section 3.0.4 describes a procedure for assaying the concentration of gaseous pollutant concentration standards and certifying that the assay concentrations are traceable to an authoritative reference concentration standard. This procedure is recommended for certifying the local working concentration standards required by the pollutant monitoring regulations of 40 CFR Part 60<sup>1,2</sup> for the calibration and audit of continuous source emission monitors. The procedure covers certification of compressed gas (cylinder) standards for CO, CO<sub>2</sub>, NO, NO<sub>2</sub>, and SO<sub>2</sub> (Procedure G1).

4.0.2 Reference Standards

Part 60 of the monitoring regulations<sup>1,2</sup> require that working standards used for calibration and audit of continuous source emission monitors be traceable to either a National Bureau of Standards (NBS) gaseous Standard Reference Material (SRM) or a NBS/EPA-approved Certified Reference Material (CRM)<sup>3</sup>. Accordingly, the reference standard used for assaying and certifying a working standard for these purposes must be an SRM, a CRM, or a suitable intermediate standard (see the next paragraph). SRM cylinder gas standards available from NBS are listed in Table 7.2 at the end of subsection 4.0. A current list of CRM cylinder gases and CRM vendors is available from the Quality Assurance Division (MD-77), Environmental Monitoring Systems Laboratory, U. S. EPA, Research Triangle Park, NC 27711.

The EPA regulations define a "traceable" standard as one which "...has been compared and certified, either directly or via not more than one intermediate standard, to a primary standard such as a...NBS [gaseous] SRM or...CRM"<sup>4,5</sup>. Certification of a working standard directly to an SRM or CRM primary standard is, of course, preferred and recommended because of the lower error. However, an intermediate reference standard is permitted, if necessary. In particular, a Gas Manufacturer's Intermediate Standard (see subsection 4.0.2.1) that has been referenced directly to an SRM or a CRM according to Procedure G1 is an acceptable intermediate standard and could be used as the reference standard on that basis. However, purchasers of com-

mercial gas standards referenced to an intermediate standard such as a GMIS should be aware that, according to the above definition, such a standard would have to be used directly for calibration or audit. Since a second intermediate standard is not permitted, such a standard could not be used as a reference standard to certify other standards.

**4.0.2.1 Gas Manufacturer's Intermediate Standard (GMIS).** A GMIS is a compressed (cylinder) gas standard that has been assayed with direct reference to an SRM or CRM and certified according to Procedure G1, and also meets the following requirements:

1. A candidate GMIS must be assayed a minimum of three (3) times, uniformly spaced over a three (3) month period.
2. Each of the three (or more) assays must be within 1.0 percent of the mean of the three (or more) assays.
3. The difference between the last assay and the first assay must not exceed 1.5 percent of the mean of the three (or more) assays.
4. The GMIS must be recertified every three months, and the reassay must be within 1.5 percent of the previous certified assay. The recertified concentration of the GMIS is the mean of the previous certified concentration and the reassay concentration.

**4.0.2.2 Recertification of Reference Standards.** Recertification requirements for SRMs and CRMs are specified by NBS and NBS/EPA, respectively. See 4.0.2.1 for GMIS recertification requirements.

#### 4.0.3 Using the Procedure

The assay/certification procedure described here is carefully designed to minimize both systematic and random errors in the assay process. Therefore, the procedure should be carried out as closely as possible to the way it is described. Similarly, the assay apparatus has been specifically designed to minimize errors and should be configured as closely as possible to the design specified. Good laboratory practice should be observed in the selection of inert materials (e.g. Teflon, stainless steel, or glass, if possible) and clean, non-contaminating components for use in portions of the apparatus in contact with the candidate or reference gas concentrations.

#### 4.0.4 Certification Documentation

Each assay/certification must be documented in a written certification report signed by the analyst and containing at least the following information:

1. Identification number (cylinder number).
2. Certified concentration of the standard, in ppm or mole percent.
3. Balance gas in the standard mixture.

4. Cylinder pressure at certification.
5. Date of the assay/certification.
6. Certification expiration date (see 4.0.6.3).
7. Identification of the reference standard used: SRM number, cylinder number, and concentration for an SRM; cylinder number and concentration for a CRM or GMIS.
8. Statement that the assay/certification was performed according to this Section 3.0.4.
9. Identification of the laboratory where the standard was certified and the analyst who performed the certification.
10. Identification of the gas analyzer used for the certification, including the make, model, serial number, the measurement principle, and the date of the last multipoint calibration.
11. All analyzer readings used during the assay/certification and the calculations used to obtain the reported certified value.
12. Chronological record of all certifications for the standard.

Certification concentrations should be reported to 3 significant digits. Certification documentation should be maintained for at least 3 years.

#### 4.0.5 Certification Label

A label or tag bearing the information described in items 1 through 9 of subsection 4.0.4 must be attached to each certified gas cylinder.

#### 4.0.6 Assay/Certification of Compressed Gas (Cylinder) Standards

4.0.6.1 Aging of newly-prepared gas standards. Freshly prepared gas standard concentrations and newly filled gas cylinders must be aged before being assayed and certified. SO<sub>2</sub> concentrations contained in steel cylinders must be aged at least 15 days; other standards must be aged at least 4 days.

4.0.6.2 Stability test for reactive gas standards. Reactive gas standards, including nitric oxide (NO), nitrogen dioxide (NO<sub>2</sub>), sulfur dioxide (SO<sub>2</sub>), and carbon monoxide (CO), that have not been previously certified must be tested for stability as follows: Reassay the concentration at least 7 days after the first assay and compare the two assays. If the second assay differs from the first assay by 1.5% or less, the cylinder may be considered stable, and the mean of the two assays should be reported as the certified concentration. Otherwise, age the cylinder for a week or more and repeat the test, using the second and third assays as if they were the first and second assays. Cylinders that are not stable may not be sold and/or used for calibration or audit purposes.

**4.0.6.3 Recertification of compressed gas standards.** Compressed gas standards must be recertified according to this Section 3.0.4 within the time limits specified in Table 7.1<sup>3,6,7</sup>. The re-assay concentration must be within 5% of the previous certified concentration. If not, the cylinder must be retested for stability (subsection 4.0.6.2). The certified concentration of a recertified standard should be reported as the mean of all assays, unless a clear trend or substantial change suggests that previous assays are no longer valid.

Table 7.1 Recertification limits for compressed gas standards.

Pollutant	Balance gas	Concentration range	Maximum months until recertification for cylinder material:	
			Al or SS	other
Carbon monoxide	N <sub>2</sub> or air	≥ 5 ppm	18	6
Nitric oxide	N <sub>2</sub>	≥ 10 ppm	18	6
Sulfur dioxide	N <sub>2</sub>	≥ 10 ppm	18	6
Nitrogen dioxide	N <sub>2</sub> or air	≥ 10 ppm	6	6
Carbon dioxide	N <sub>2</sub> or air	≥ 300 ppm	18	18
Oxygen	N <sub>2</sub>	≥ 2 percent	18	18
Sulfur dioxide and carbon dioxide	N <sub>2</sub>	≥ 200 ppm SO <sub>2</sub> , ≥ 10 percent CO <sub>2</sub>	18	6
Propane	N <sub>2</sub> or air	≥ 5 ppm	18	6
Others not specifically listed			6	6

**4.0.6.4 Minimum cylinder pressure.** No compressed gas cylinder standard should be used when its gas pressure is below 700 kPa (100 psi), as indicated by the cylinder pressure gauge.

**4.0.6.5 Assay/certification of multi-component compressed gas standards.** Procedure G1 may be used to assay and certify individual components of multi-component gas standards, provided that none of the components other than the component being assayed cause a detectable response on the analyzer.

#### 4.0.7 Analyzer Calibration

4.0.7.1 Basic analyzer calibration requirements. The assay procedure described in this Section 3.0.4 employs a direct ratio referencing technique that inherently corrects for minor analyzer calibration variations (drift) and DOES NOT depend on the absolute accuracy of the analyzer calibration. What is required of the analyzer is as follows: 1) it must have a linear response to the pollutant of interest (see subsection 4.0.7.5), 2) it must have good resolution and low noise, 3) its response calibration must be reasonably stable during the assay/certification process, and 4) all assay concentration measurements must fall within the calibrated response range of the analyzer.

4.0.7.2 Analyzer multipoint calibration. The gas analyzer used for the assay/certification must have had a multipoint calibration within 3 months of its use when used with this procedure. This calibration is not used to quantitatively interpret analyzer readings during the assay/certification of the candidate gas because a more accurate, direct ratio comparison of the candidate concentration to the reference standard concentration is used. However, this multipoint calibration is necessary to establish the calibrated range of the analyzer and its response linearity.

The multipoint calibration should consist of analyzer responses to at least 5 concentrations, including zero, approximately evenly spaced over the concentration range. Analyzer response units may be volts, millivolts, percent of scale, or other measurable analyzer response units. The upper range limit of the calibrated range is determined by the highest calibration point used. If the analyzer has a choice of concentration ranges, the optimum range for the procedure should be selected and calibrated. Plot the calibration points and compute the linear regression slope and intercept. See subsection 4.0.7.5 for linearity requirements and the use of a mathematical transformation, if needed. The intercept should be less than 1 percent of the upper concentration range limit, and the correlation coefficient ( $r$ ) should be at least 0.999.

4.0.7.3 Zero and span check and adjustment. On each day that the analyzer will be used for assay/certification, its response calibration must be checked with a zero and at least one span concentration near the upper concentration range limit. If necessary, the zero and span controls of the analyzer should be adjusted so that the analyzer's response (i.e. calibration slope) is within about  $\pm 5$  percent of the response indicated by the most recent multipoint calibration. If a zero or span adjustment is made, allow the analyzer to stabilize for at least an hour or more before beginning the assay procedure, since some analyzers drift for a period of time following zero or span adjustment. If the analyzer is not in continuous operation, turn it on and allow it to stabilize for at least 12 hours before the zero and span check.

4.0.7.4 Pollutant standard for multipoint calibration and zero and span adjustment. The pollutant standard or standards used for multipoint calibration or zero and span checks or adjustments must be obtained from a compressed gas standard certified traceable to an NBS SRM or a NBS/EPA CRM according to Procedure G1 of this Section 3.0.4. This standard need not be the same as the reference standard used in the assay/certification. The zero gas must meet the requirements in subsection 4.0.8.

**4.0.7.5 Linearity of analyzer response.** The direct ratio assay technique used in Procedure G1 requires that the analyzer have a linear response to concentration. Linearity is determined by comparing the quantitative difference between a smoothly-drawn calibration curve based on all calibration points and a straight line drawn between zero and an upper reference point (see Figure 1). This difference is measured in concentration units, parallel to the concentration axis, from a point on the calibration curve to the corresponding point for the same response on the straight line.

For the general linearity requirement, the straight line is drawn between zero and the highest calibration point (Figure 1a). Linearity is then acceptable when no point on the smooth calibration curve deviates from the straight line by more than 1.5 percent of the value of the highest calibration concentration. An alternative linearity requirement is defined on the basis of the actual reference and candidate concentrations to be used for the assay. In this case, the reference and candidate concentrations are plotted on the calibration curve, and the straight line is drawn from zero to the reference concentration and extrapolated, if necessary, beyond the candidate concentration (Figure 1b). The deviation of the smooth calibration curve from the straight line at the candidate concentration point then must not exceed 0.8 percent of the value of the reference concentration. This latter specification may allow the use of an analyzer having greater nonlinearity when the reference and candidate concentrations are nearly the same.

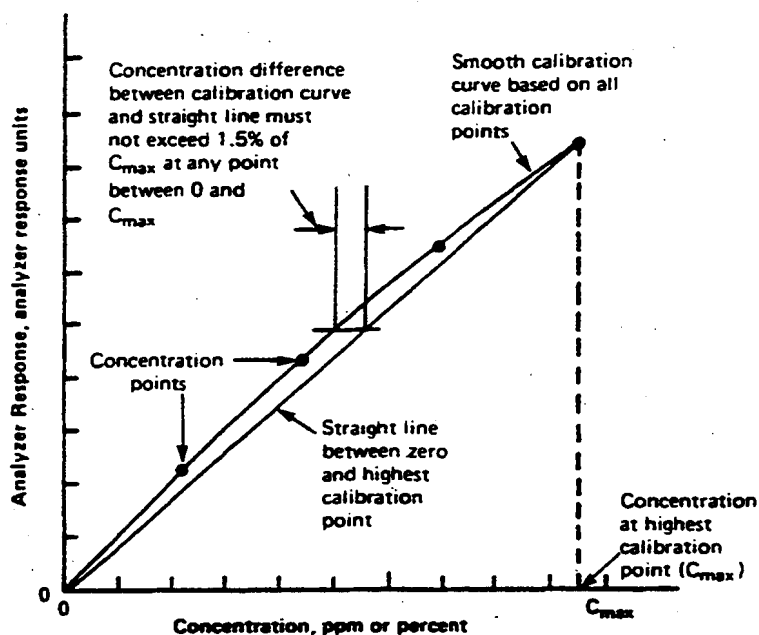
For analyzers having an inherently non-linear response, the response can usually be linearized with a simple mathematical transformation of the response values, such as  $R' = \text{square root}(R)$  or  $R' = \log(R)$ , where  $R'$  is the transformed response value and  $R$  is the actual analyzer response value. Using the transformed response values, the multipoint calibration should meet one of the above linearity requirements as well as the requirements for intercept and correlation coefficient given in subsection 4.0.7.2.

#### 4.0.8 Zero Gas

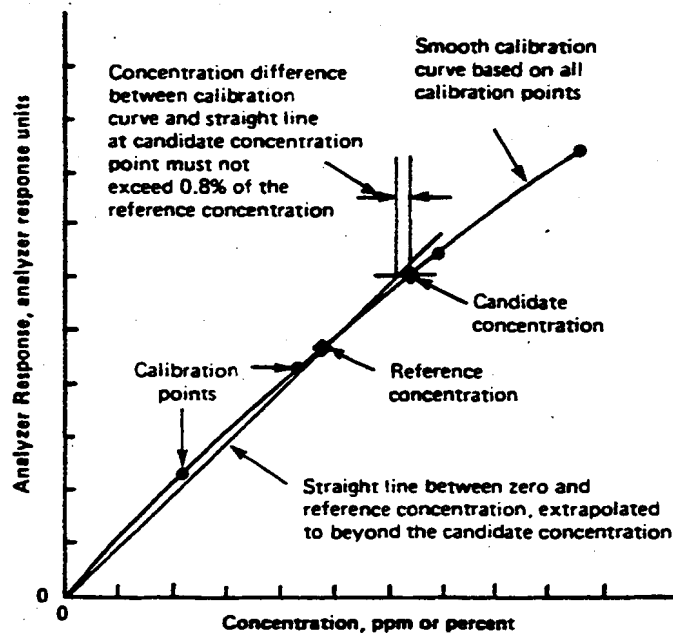
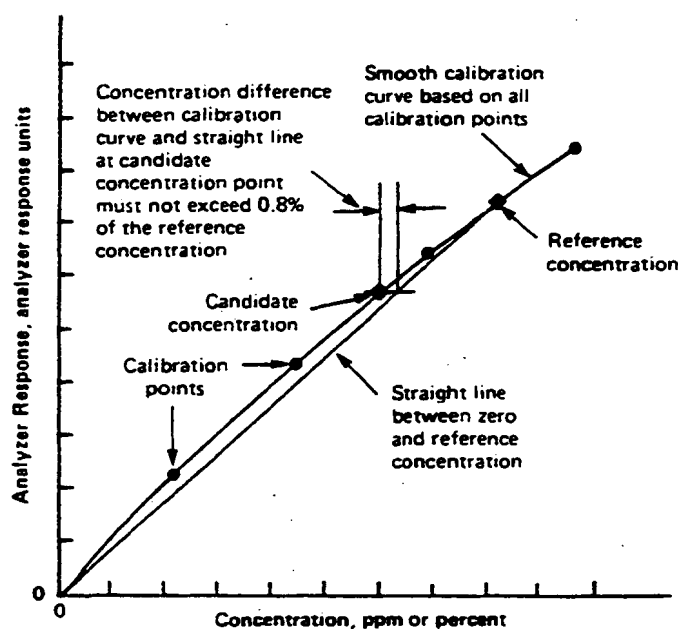
Zero gas used for dilution of any candidate or reference standard should be clean, dry, zero-grade air or nitrogen containing a concentration of the pollutant of interest equivalent to less than 0.5 percent of the analyzer's upper range limit concentration. The zero gas also should contain no contaminant that causes a detectable response on the analyzer or that suppresses or enhances the analyzer's response to the pollutant. The oxygen content of zero air should be the same as that of ambient air.

#### 4.0.9 Accuracy Assessment of Commercially Available Standards

Periodically, the USEPA will assess the accuracy of commercially available compressed gas standards that have been assayed and certified according to this Section 3.0.4. Accuracy will be assessed by EPA audit analysis of representative actual commercial standards obtained via an anonymous agent. The accuracy audit results, identifying the actual gas manufacturers or vendors, will be published as public information.



a) General linearity requirement



b) Alternative linearity requirement

Figure 1. Illustration of linearity requirements.

Table 7.2. NBS SRM reference gases.

SRM number	Type	Nominal concentration		SRM number	Type	Nominal concentration	
2627	NO/N <sub>2</sub>	5	ppm	1693	SO <sub>2</sub> /N <sub>2</sub>	50	ppm
2628	NO/N <sub>2</sub>	10	ppm	1694	SO <sub>2</sub> /N <sub>2</sub>	100	ppm
2629	NO/N <sub>2</sub>	20	ppm	1661a	SO <sub>2</sub> /N <sub>2</sub>	500	ppm
1683b	NO/N <sub>2</sub>	50	ppm	1662a	SO <sub>2</sub> /N <sub>2</sub>	1000	ppm
1684b	NO/N <sub>2</sub>	100	ppm	1663a	SO <sub>2</sub> /N <sub>2</sub>	1500	ppm
1685b	NO/N <sub>2</sub>	250	ppm	1664a	SO <sub>2</sub> /N <sub>2</sub>	2500	ppm
1686b	NO/N <sub>2</sub>	500	ppm	1696	SO <sub>2</sub> /N <sub>2</sub>	3500	ppm
1687b	NO/N <sub>2</sub>	1000	ppm				
2630	NO/N <sub>2</sub>	1500	ppm	1670	CO <sub>2</sub> /Air	330	ppm
2631	NO/N <sub>2</sub>	3000	ppm	1671	CO <sub>2</sub> /Air	340	ppm
				1672	CO <sub>2</sub> /Air	350	ppm
2653	NO <sub>2</sub> /Air	250	ppm				
2654	NO <sub>2</sub> /Air	500	ppm	2632	CO <sub>2</sub> /N <sub>2</sub>	300	ppm
2655	NO <sub>2</sub> /Air	1000	ppm	2633	CO <sub>2</sub> /N <sub>2</sub>	400	ppm
2656	NO <sub>2</sub> /Air	2500	ppm	2634	CO <sub>2</sub> /N <sub>2</sub>	800	ppm
				2619a	CO <sub>2</sub> /N <sub>2</sub>	0.5	percent
2612a	CO/Air	10	ppm	2620a	CO <sub>2</sub> /N <sub>2</sub>	1.0	percent
2613a	CO/Air	20	ppm	2621a	CO <sub>2</sub> /N <sub>2</sub>	1.5	percent
2614a	CO/Air	45	ppm	2622a	CO <sub>2</sub> /N <sub>2</sub>	2.0	percent
				2623a	CO <sub>2</sub> /N <sub>2</sub>	2.5	percent
1677c	CO/N <sub>2</sub>	10	ppm	2624a	CO <sub>2</sub> /N <sub>2</sub>	3.0	percent
2635	CO/N <sub>2</sub>	25	ppm	2625a	CO <sub>2</sub> /N <sub>2</sub>	3.5	percent
1678c	CO/N <sub>2</sub>	50	ppm	2626a	CO <sub>2</sub> /N <sub>2</sub>	4.0	percent
1679c	CO/N <sub>2</sub>	100	ppm	1674b	CO <sub>2</sub> /N <sub>2</sub>	7.0	percent
2636	CO/N <sub>2</sub>	250	ppm	1675b	CO <sub>2</sub> /N <sub>2</sub>	14.0	percent
1680c	CO/N <sub>2</sub>	500	ppm				
1681c	CO/N <sub>2</sub>	1000	ppm	1665b	C <sub>3</sub> H <sub>8</sub> /Air	3	ppm
2637	CO/N <sub>2</sub>	2500	ppm	1666b	C <sub>3</sub> H <sub>8</sub> /Air	10	ppm
2638	CO/N <sub>2</sub>	5000	ppm	1667b	C <sub>3</sub> H <sub>8</sub> /Air	50	ppm
2639	CO/N <sub>2</sub>	1	percent	1668b	C <sub>3</sub> H <sub>8</sub> /Air	100	ppm
2640	CO/N <sub>2</sub>	2	percent	1669b	C <sub>3</sub> H <sub>8</sub> /Air	500	ppm
2641	CO/N <sub>2</sub>	4	percent				
2642	CO/N <sub>2</sub>	8	percent	2643	C <sub>3</sub> H <sub>8</sub> /N <sub>2</sub>	100	ppm
				2644	C <sub>3</sub> H <sub>8</sub> /N <sub>2</sub>	250	ppm
2657	O <sub>2</sub> /N <sub>2</sub>	2	percent	2645	C <sub>3</sub> H <sub>8</sub> /N <sub>2</sub>	500	ppm
2658	O <sub>2</sub> /N <sub>2</sub>	10	percent	2646	C <sub>3</sub> H <sub>8</sub> /N <sub>2</sub>	1000	ppm
2659	O <sub>2</sub> /N <sub>2</sub>	21	percent	2647	C <sub>3</sub> H <sub>8</sub> /N <sub>2</sub>	2500	ppm
				2648	C <sub>3</sub> H <sub>8</sub> /N <sub>2</sub>	5000	ppm
				2649	C <sub>3</sub> H <sub>8</sub> /N <sub>2</sub>	1	percent
				2650	C <sub>3</sub> H <sub>8</sub> /N <sub>2</sub>	2	percent

NBS-SRM cylinders contain approximately 870 liters of gas at STP.

For availability, contact: Office of Standard Reference Materials  
Chemistry Building, Room B311  
NBS, Gaithersburg, Maryland 20899  
(301) 975-6776. (FTS 879-6776)

#### 4.1 PROCEDURE G1: ASSAY AND CERTIFICATION OF A COMPRESSED GAS STANDARD WITHOUT DILUTION

##### 4.1.1 Applicability

This procedure may be used to assay the concentration of a candidate compressed gas (cylinder) pollutant standard, based on the concentration of a compressed gas (cylinder) reference standard of the same pollutant compound, and certify that the assayed concentration thus established for the candidate standard is traceable to the reference standard. The procedure employs a pollutant gas analyzer to compare the candidate and reference gas concentrations by direct measurement--without dilution of either gas--to minimize assay error.

##### 4.1.2 Limitations

1. The concentration of the candidate gas standard must be between 0.3 and 1.3 times the concentration of the reference gas standard.
2. The analyzer must have a calibrated range capable of directly measuring both the candidate and the reference gas concentrations.
3. The analyzer's response (or transformed response) must be linear with respect to concentration.
4. The balance gas in both the candidate and reference standards must be identical, unless it can be shown that the analyzer is insensitive to any difference in the balance gases.
5. A source of clean, dry zero gas is required.

##### 4.1.3 Assay Apparatus

Figure G1 illustrates the relatively simple assay apparatus. The configuration is designed to allow convenient routing of the zero gas and undiluted samples of the reference gas and candidate gases, in turn, to the analyzer for measurement, as selected by three-way valves V1 and V2. Pressure regulators and needle valves (V3 and V4) control the individual gas flows. The pollutant concentrations are delivered to the analyzer via a vented tee, which discharges excess flow and insures that the assay concentrations sampled by the analyzer are always at a fixed (atmospheric) pressure. A small, uncalibrated rotameter monitors the vent flow to verify that the total gas flow rate exceeds the sample flow rate demand of the analyzer so that no room air is admitted through the vent. Valves V1 and V2 could be replaced by a single four-way valve (with 3 inputs and 1 output) or by manually moving the output connection to each of the gases as needed. See also subsection 4.0.3.

##### 4.1.4 Analyzer

See subsection 4.0.7.1. The pollutant gas analyzer must have a linear response function and a calibrated range capable of measuring the full concentration of both the candidate and the reference gas standards directly, without dilution. It must

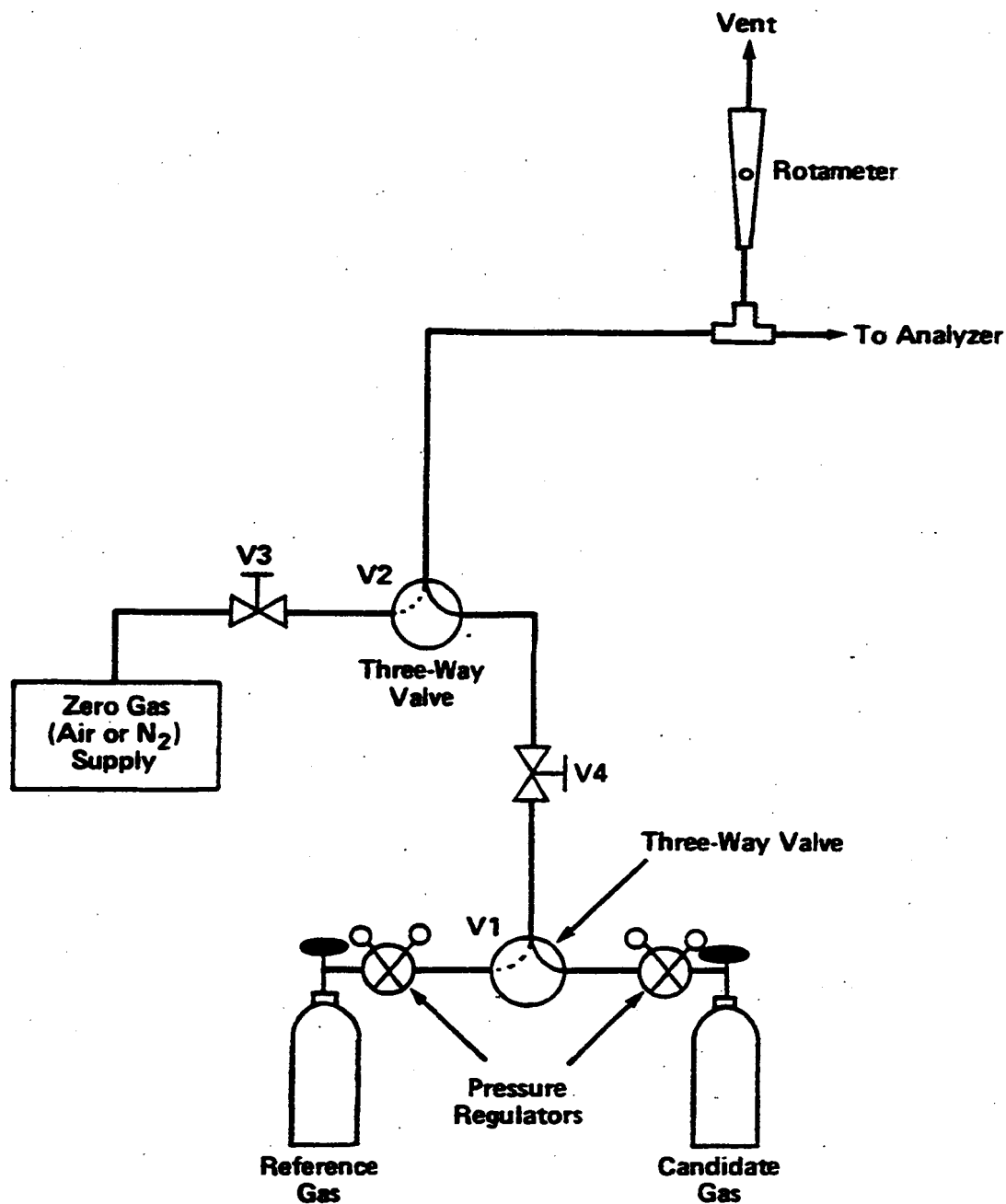


Figure G1. Suggested assay apparatus for Procedure G1.

have good resolution (readability), good precision, a stable response, and low output signal noise. In addition, the analyzer must have good specificity for the pollutant of interest so that it has no detectable response to any contaminant that may be contained in either the candidate or reference gas. If the candidate and reference gases contain dissimilar balance gases (air versus nitrogen or different proportions of oxygen in the balance air, for example), the analyzer must be proven to be insensitive to the two different balance gases. This may be accomplished by showing no difference in analyzer response when measuring pollutant concentrations diluted with identical flow rates of the two balance gases.

The analyzer should be connected to a suitable, precision chart recorder or other data acquisition device to facilitate graphical observation and documentation of the analyzer responses obtained during the assay.

#### 4.1.5 Analyzer Calibration

4.1.5.1 Multipoint calibration. See subsections 4.0.7.2 and 4.0.7.4.

4.1.5.2 Calibration range. The calibrated range of the analyzer must include both the candidate and reference gas concentrations, such that the higher concentration does not exceed 97 percent of the upper range limit, and the lower concentration is not below 25 percent of the upper range limit (assuming a lower range limit of zero). Within these limits, select a calibrated analyzer range that will produce the highest analyzer responses.

4.1.5.3 Linearity. The direct ratio assay technique used in this procedure requires that the analyzer have a linear response to concentration (see subsection 4.0.7.5). High-concentration-range analyzers of the type that are required for this procedure may not be inherently linear, but they usually have a predictable, non-linear response characteristic that can be mathematically transformed to produce a sufficiently linear response characteristic suitable for use in this procedure. Any such response transformation should be verified by using it for the multipoint calibration. Caution should be exercised in using a transformed response curve because physical zero or span adjustments to the analyzer may produce unexpected effects on the transformed characteristic.

4.1.5.4 Zero and span adjustment. See subsections 4.0.7.3 and 4.0.7.4. Prior to carrying out the assay/certification procedure, check the calibration of the analyzer and, if necessary, adjust the analyzer's zero and span controls to re-establish the response characteristic determined at the most recent multipoint calibration. Allow the analyzer to stabilize for an hour or more after any zero or span adjustment. If there is any doubt that a transformed response characteristic is still linear following a zero or span adjustment, verify linearity with a multipoint calibration (subsection 4.0.7.2) using at least 3 known pollutant concentrations, including zero.

#### 4.1.6 Assay Gases

4.1.6.1 Candidate gas standard. See subsections 4.0.6 and 4.1.2.

4.1.6.2 Reference gas standard. See subsections 4.0.2, 4.1.2, and 4.0.6.4. Select a reference standard such that the concentration of the candidate gas is not

more than 30 percent above nor less than 70 percent below the concentration the standard.

4.1.6.3 Zero gas. See subsection 4.0.8. The zero gas should match the balance gas used in the cylinder concentrations.

#### 4.1.7 Assay Procedure

1. Verify that the assay apparatus is properly configured, as described in subsection 4.1.3 and shown in Figure G1.
2. Verify that the linearity of the analyzer has been checked within the last 3 months (see subsections 4.0.7.2, 4.0.7.5, and 4.1.4), that the zero and span are adjusted correctly (subsection 4.0.7.3), that the candidate and reference gas concentrations are within 25 and 97 percent of the upper range limit of the calibrated measurement range of the analyzer, and that the analyzer is operating stably.
3. Adjust the flow rates of the three gases (reference, candidate, and zero) to approximately the same value that will provide enough flow for the analyzer and sufficient excess to assure that no ambient air will be drawn into the vent.
4. Conduct a triad of measurements with the analyzer. Each triad consists of a measurement of the zero gas concentration, a measurement of the reference gas concentration, and a measurement of the candidate gas concentration. Use valve V1 and V2 to select each of the three concentrations for measurement. For each measurement, allow ample time for the analyzer to achieve a stable response reading. Record the stable analyzer response for each measurement, using the same response units (volt, millivolts, percent of scale, etc.) used for the multipoint calibration and any transformation of the response readings necessary for linearity. Do not translate the response readings to concentration values via the calibration curve (see the footnote following Equation G1). Do not make any zero, span, or other physical adjustments to the analyzer during the triad of measurements.
5. Conduct at least 2 additional measurement triads, similar to step 4 above. However, for these subsequent triads, change the order of the three measurements (e.g. measure reference gas, zero gas, candidate gas for the second triad and zero gas, candidate gas, reference gas for the third triad, etc.).
6. If any one or more of the measurements of a triad is invalid or abnormal for any reason, discard all three measurements of the triad and repeat the triad.
7. For each triad of measurements, calculate the assay concentration of the candidate gas as follows:

$$C_c = C_r \frac{R_c - R_z}{R_r - R_z} \quad \text{Equation G1}$$

where:  $C_C$  = Assay concentration of the candidate gas standard, ppm or percent;  
 $C_R$  = Concentration of the reference gas standard, ppm or percent;  
 $R_C$  = Stable response reading of the analyzer for the candidate gas, analyzer response units;\*  
 $R_Z$  = Stable response reading of the analyzer for the zero gas, analyzer response units;\*  
 $R_R$  = Stable response reading of the analyzer for the reference gas, analyzer response units.\*

\*Analyzer response units are the units used to express the direct response readings of the analyzer, such as volts, millivolts, percent of scale, etc. DO NOT convert these direct response readings to concentration units with the multipoint calibration curve or otherwise adjust these readings except for transformation necessary to achieve response linearity.

8. Calculate the mean of the 3 (or more) valid assays. Calculate the percent difference of each assay from the mean. If any one of the assay values differs from the mean by more than 1.5%, discard that assay value and conduct another triad of measurements to obtain another assay value. When at least 3 assay values all agree within 1.5% of their mean, report the mean value as the certified concentration of the candidate gas standard. For newly-prepared reactive standards, a reassay at least 7 days later is required to check the stability of the standard; see subsection 4.0.6.2.

#### 4.1.8 Stability Test for Newly-Prepared Standards

See subsections 4.0.6.1 and 4.0.6.2.

#### 4.1.9 Certification Documentation

See subsections 4.0.4 and 4.0.5.

#### 4.1.10 Recertification Requirements

See subsections 4.0.6.3 and 4.0.6.4.

#### 4.2 References.

1. Code of Federal Regulations, Title 40, Part 60, "Standards of Performance for New Stationary Sources," Appendix A, Method 20 (1982).
2. Standards of Performance for New Stationary Sources; Quality Assurance Requirements for Gaseous Continuous Emission Monitoring Systems Used for Compliance Determination, promulgated in the Federal Register, June 4, 1987, pp. 21003-21010.
3. "A Procedure for Establishing Traceability of Gas Mixtures to Certain National Bureau of Standards Standard Reference Materials. EPA-600/7-81-010. Joint publication by NBS and EPA, May 1981. Available from the U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory (MD-77), Research Triangle Park, NC 27711.
4. Code of Federal Regulations, Title 40, Part 50, "National Ambient Air Quality Measurement Methodology".
5. Code of Federal Regulations, Title 40, Part 58, "Ambient Air Quality Surveillance," Appendixes A and B.
6. Shores, R. C. and F. Smith, "Stability Evaluation of Sulfur Dioxide, Nitric Oxide, and Carbon Monoxide Gases in Cylinders. NTIS No. PB 85-122646. Available from the National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161.
7. Method 6A and 6B, "Determination of Sulfur Dioxide, Moisture, and Carbon Dioxide Emissions from Fossil Fuel Combustion Sources," Quality Assurance Handbook for Air Pollution Measurement Systems, Volume III, Section 3.13.8, July 1986. Available from the U.S. Environmental Protection Agency, Center for Environmental Research Information, Cincinnati, OH 45268.
8. "List of Designated Reference and Equivalent Methods." Current edition available from the U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Quality Assurance Division (MD-77), Research Triangle Park, NC 27711.